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(21) International Application Number: PCT/US91/06686 (22) International Filing Date: 13 September 1991 (13.09.91) (30) Priority data: 602,738 24 October 1990 (24.10.90) US (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 33427 (US). (72) Inventors: IQBAL, Mohammad ; MILLER, Alan, G. ; SMITH, Terrance, P. ; STOFKO, John, J., Jr. ; P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		(74) Agents: WEINSTEIN, David, L. et al.; Minnesota Mining and Manufacturing Company, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). (81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: COATING OF HYDROPHILIC INTERPENETRATING NETWORKS			
(57) Abstract			
<p>This invention relates to transparent materials that are capable of absorbing liquids, and, more particularly, to materials that can be used as ink-receptive layers for transparent imageable materials. Compositions useful as transparent liquid absorbent materials have been formed by blending a liquid-insoluble polymeric material with a liquid-soluble polymeric material. The liquid-insoluble material is presumed to form a matrix, within which the liquid soluble material resides. A problem that frequently arises in the formulation of polymer blends is the incompatibility of the polymers being blended. When attempts are made to blend polymers that are incompatible, phase separation occurs, resulting in haze, lack of transparency, and other forms of non-homogeneity. This invention provides polymeric networks comprising blends of polymers wherein at least one of the polymers of the blend is crosslinked, after blending, to form a continuous network throughout the bulk of the blend, the uncrosslinked components of the blend being intertwined in such a way as to form a macroscopically homogeneous composition. Substantially all of the crosslinking occurs after the polymeric blend is coated and dried to a continuous film in contrast to crosslinking in solution, thereby providing an easily coatable solution without gelation. The integrity of such networks persist even after absorption of solvent. These materials can be used to form durable, non-tacky, ink-absorbent, transparent coatings for graphical materials.</p>			
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⁺ Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

COATING OF HYDROPHILIC INTERPENETRATING NETWORKSBackground of the Invention

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1. Field of the Invention

This invention relates to transparent materials that are capable of absorbing liquids, and, more particularly, to materials that can be used as ink-receptive layers for transparent imageable materials.

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2. Discussion of the Art

Transparent materials that are capable of absorbing significant quantities of liquid, while maintaining some degree of durability and transparency, are useful in contact lenses, priming layers for coatings coated out of aqueous solutions, fog-resistant coatings, and transparent imageable materials for use with mechanized ink depositing devices, such as pen plotters and ink-jet printers. Transparent imageable materials are used as overlays in technical drawings and as transparencies for overhead projection. It is desirable that the surface of liquid absorbent materials for use in transparent graphical applications be tack free to the touch even after absorption of significant quantities of ink.

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During normal use of pen plotters and ink-jet printers, the inks used in such machines are exposed to open air for long periods of time prior to imaging. After such exposure to air, the ink must still function in an acceptable manner, without loss of solvent. To meet this requirement, ink formulations typically utilize solvents of very low volatility, such as water, ethylene glycol, propylene glycol, and so on. Inks that contain water or

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water-miscible solvents are commonly referred to as aqueous inks, and the solvents for these inks are commonly referred to as aqueous liquids.

5 Because of the low volatility of aqueous liquids, drying of an image by means of evaporation is very limited. In the case of imaging onto a paper sheet, which has a fibrous nature, a significant amount of the liquid diffuses into the sheet, and the surface appears dry to the touch within a very short time. In the case of
10 imaging onto polymeric film, some means of absorbing aqueous liquids is needed if satisfactory drying of the image is to occur.

Compositions useful as transparent liquid absorbent materials have been formed by blending a liquid-insoluble polymeric material with a liquid-soluble
15 polymeric material. The liquid-insoluble material is presumed to form a matrix, within which the liquid soluble material resides. Examples of such blends are the transparent water-absorbent polymeric materials disclosed in U.S. Patent Nos. 4,300,820 and 4,369,229, and in
20 European Patent Application No. 0 233 703.

Because of the low volatility of aqueous liquids, drying of an image by means of evaporation is very limited. In the case of imaging onto a paper sheet which has a fibrous nature, a significant amount of the
25 liquid diffuses into the sheet, and the surface appears dry to the touch within a very short time. In the case of imaging onto polymeric film, some means of absorbing aqueous liquids is needed if satisfactory drying of the image is to occur.

30 A problem that frequently arises in the formulation of polymer blends is the incompatibility of the polymers being blended. When attempts are made to blend polymers that are incompatible, phase separation occurs, resulting in haze, lack of transparency, and other
35 forms of inhomogeneity.

Compatibility between two or more polymers in a blend can often be improved by incorporating into the liquid-insoluble matrix-forming polymer chains monomeric units that exhibit some affinity for the liquid-soluble polymer. Polymeric materials having even a small amount of acid functionality are more likely to exhibit compatibility with polyvinyl lactams. Generally, the compatibility of polymers being blended is improved if the polymers are capable of hydrogen bonding to one another.

A second form of incompatibility noted in using blends of liquid-absorbent polymers is the incompatibility of the matrix forming insoluble polymer with the liquid being absorbed. For example, if the liquid being absorbed is water, and if the water-insoluble polymers are hydrophobic, some inhibition of water absorption ability can be expected. One method of overcoming this difficulty is to utilize hydrophilic matrix polymers that are water-insoluble at the temperatures at which they are to be used, though they may be water-soluble at a different temperature. In U.S. Patent No. 4,503,111, ink-receptive coatings comprising either polyvinyl alcohol or gelatin blended with polyvinyl pyrrolidone are disclosed. Both polyvinyl alcohol and gelatin, being water-insoluble at room temperature, are able to act as matrix-forming polymers for these coatings, and the coatings are quite receptive to aqueous inks. However, the coatings do exhibit a tendency to become tacky, either because of imaging, or because of high humidity.

It therefore becomes clear that while blends of soluble and insoluble polymers may be useful as liquid absorbent compositions, they suffer major limitations in liquid absorption ability and in durability.

Summary of the Invention

This invention provides a coatable composition capable of forming hydrophilic liquid-absorbent, semi-interpenetrating networks, hereinafter referred to as

SIPNs. The SIPNs of this invention are formed from polymer blends comprising (a) at least one crosslinkable polymer, (b) at least one liquid-absorbent polymer comprising a water-absorbent polymer, and (c) optionally, a crosslinking agent. Substantially all crosslinking of the crosslinkable polymer takes place after the composition is coated onto a substrate and allowed to dry. These SIPNs are continuous networks wherein the crosslinked polymer forms a continuous matrix throughout the bulk of the material and through which the liquid-absorbent polymer is intertwined in such a way as to form a macroscopically homogeneous composition. The SIPNs of this invention are capable of absorbing significant quantities of those liquids that are solvents or swelling agents of the uncrosslinked portion of the SIPN without loss of physical integrity and without leaching or other forms of phase separation. In cases where the SIPNs are initially transparent, they also remain transparent after absorption of significant quantities of liquids.

The nature of the crosslinking used in the formation of the matrix component SIPN is such that it provides durability in the presence of the liquids encountered during use with compatibility toward the liquid-absorbent component. The crosslinked matrix component and the liquid-absorbent component are miscible, exhibit little or no phase separation, and generate little or no haze upon coating. The nature of the crosslinking should not cause phase separation or other inhomogeneity in the SIPN, or gelation of coating solutions before use or coating.

The present invention further provides transparent compositions capable of providing improved ink absorption and durability, while at the same time retaining transparency and being amenable to the types of processing commonly used in producing transparent graphical materials.

Detailed Description

The crosslinked portion of the SIPN will hereinafter be called the matrix component, and the liquid-absorbent portion will hereinafter be called the absorbent component.

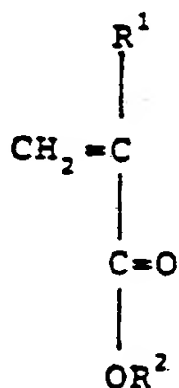
The term "hydrophilic", as used herein, is used to describe a material that is generally receptive to water, either in the sense that its surface is wettable by water or in the sense that the bulk of the material is able to absorb significant quantities of water. More specifically, materials that exhibit surface wettability by water are said to have hydrophilic surfaces, while materials that have surfaces not wettable by water will be said to have hydrophobic surfaces. The term "hydrophilic liquid-absorbing materials" as used herein, describes materials that are capable of absorbing significant quantities of water, blends of water and other liquids, including those materials that are water-soluble. When molecular structures are being discussed, monomeric units will be referred to as hydrophilic units if they have a water-sorption capacity of at least one mole of water per mole of monomeric unit. Sorption capacities of various monomeric units are given, for example, in D. W. Van Krevelin, with the collaboration of P. J. Hoftyzer, Properties of Polymers: Correlations With Chemical Structure Elsevier Publishing Company (Amsterdam, London, New York: 1972) pages 294-296. Monomeric units will be referred to as hydrophobic if they form water-insoluble polymers capable of absorbing only small amounts of water when polymerized by themselves.

The matrix component of the SIPN of the present invention comprises crosslinkable polymers that are either hydrophobic or hydrophilic in nature, and can be derived from the copolymerization of acrylic or other hydrophobic or hydrophilic ethylenically unsaturated monomeric units

with monomers having acidic groups, or if pendant ester groups are already present in these acrylic or ethylenically unsaturated monomeric units, by hydrolysis.

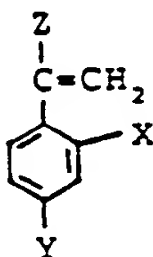
Hydrophobic monomeric units suitable for preparing crosslinkable matrix components are preferably selected from:

- (1) acrylates and methacrylates having the structure:



wherein R^1 represents H or $-CH_3$, and R^2 represents an alkyl group having up to ten carbon atoms, preferably up to four carbon atoms, and more preferably one to two carbon atoms, a cycloaliphatic group having up to nine carbon atoms, a substituted or unsubstituted aryl group having up to 14 carbon atoms, and an oxygen containing heterocyclic group having up to ten carbon atoms;

- (2) acrylonitrile or methacrylonitrile;
(3) styrene or α -methylstyrene having the structure:

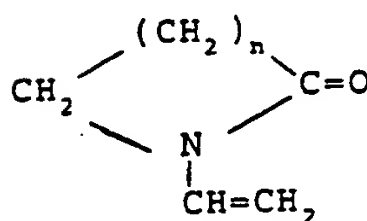


where X and Y independently represent hydrogen or alkyl groups having up to 4 carbon atoms, preferably 1 or 2 carbon atoms, a halogen atom, alkyl halide group, or OR^m where R^m represent hydrogen or an alkyl group having up to 4 carbon atoms, preferably 1 or 2 carbon atoms, and Z represents hydrogen or methyl; and

(4) vinyl acetate.

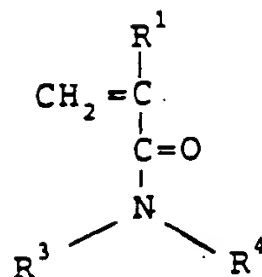
Hydrophilic monomeric units suitable for preparing crosslinkable polymers are preferably selected from:

(1) vinyl lactams having the repeating structure:



where n represents the integer 2 or 3;

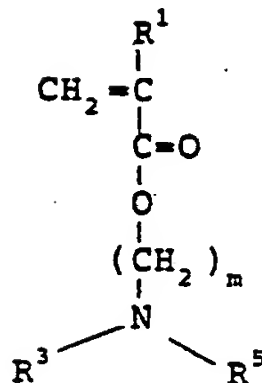
(2) acrylamide or methacrylamide having the structure:



where R^1 is as defined previously, R^3 represents H or an alkyl group having up to ten carbon atoms, preferably from one to four carbon atoms, and R^4 represents H or an alkyl group, having up to ten carbon atoms, preferably from one to four carbon

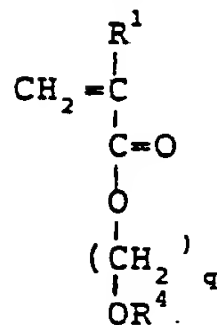
atoms, or an hydroxyalkyl group, or an alkoxy alkyl group having the structure of $-(CH_2)_p-OR^3$, where p represents an integer from 1 to 3, inclusive;

- (3) tertiary amino alkylacrylates or tertiary amino alkylmethacrylates having the structure:



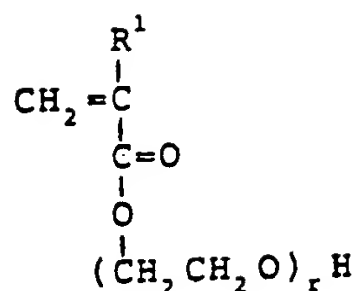
where m represents the integer 1 or 2 and R^1 and R^3 are as defined previously, and R^5 represents H or an alkyl group having up to ten carbon atoms, preferably from one to four carbon atoms;

- (4) hydroxy alkylacrylates, alkoxy alkylacrylates, hydroxy alkyl methacrylates, or alkoxy alkyl methacrylates having the structure:



where R^1 and R^4 are as defined previously, q represents an integer from 1 to 4, inclusive, preferably 2 to 3; and

- (5) alkoxy acrylates or alkoxy methacrylates having the structure:



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where r represents an integer from 5 to 25, inclusive, and R^1 is defined previously.

Some of the previously mentioned structures of both the hydrophobic and hydrophilic monomeric units contain pendant ester groups that can readily be rendered crosslinkable by hydrolysis. For the others, monomeric units containing acidic groups must be incorporated into the polymeric structure to render them crosslinkable. Polymerization of these monomers can be carried out by typical free radical solution, emulsion, or suspension polymerization techniques. Suitable monomeric units containing acidic groups include acrylic acid or methacrylic acid, other copolymerizable carboxylic acids, and ammonium salts.

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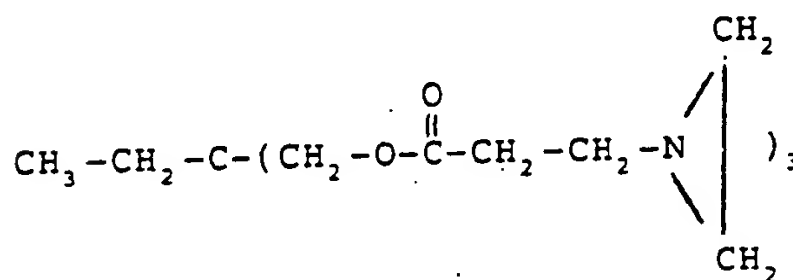
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The crosslinking agent is preferably selected from the group of polyfunctional aziridines possessing at least two crosslinking sites per molecule, such as trimethylol propane-tris-(β -(N-aziridinyl)propionate)

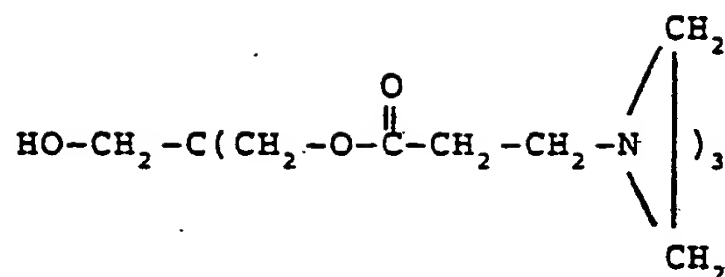
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penta erythritol-tris-(β -(N-aziridinyl)propionate)

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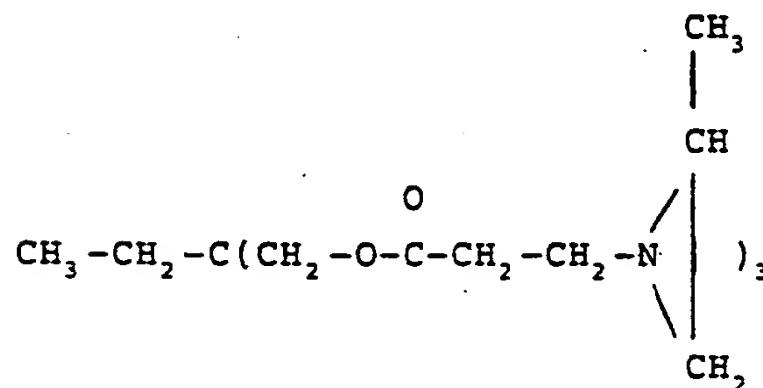
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trimethylolpropane-tris-(β -(N-methylaziridiny) propionate)

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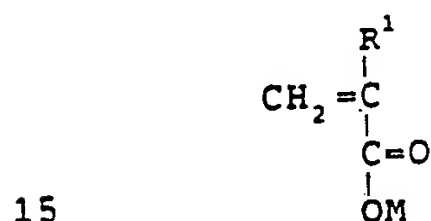
and so on. Crosslinking can also be brought about by means of metal ions, such as provided by multivalent metal ion salts, provided the composition containing the crosslinkable polymer is made from 80 to 99 parts by weight of monomer and from 1 to 20 parts by weight of a chelating compound.

The metal ions can be selected from ions of the following metals: cobalt, calcium, magnesium, chromium, aluminum, tin, zirconium, zinc, nickel, and so on, with the preferred compounds being selected from aluminum acetate, aluminum ammonium sulfate dodecahydrate, alum, aluminum chloride, chromium (III) acetate, chromium (III) chloride hexahydrate, cobalt acetate, cobalt (II) chloride hexahydrate, cobalt (II) acetate tetrahydrate, cobalt sulfate hydrate, copper sulfate pentahydrate, copper acetate hydrate, copper chloride dihydrate, ferric chloride hexahydrate, ferric ammonium sulfate dodecahydrate, ferrous chloride, tetrahydrate, magnesium acetate tetrahydrate, magnesium chloride hexahydrate, magnesium nitrate hexahydrate, manganese acetate tetrahydrate, manganese chloride tetrahydrate, nickel

chloride hexahydrate, nickel nitrate hexahydrate, stannous chloride dihydrate, stannic chloride, tin (II) acetate, tin (IV) acetate, strontium chloride hexahydrate, strontium nitrate, zinc acetate dihydrate, zinc chloride, zinc nitrate, zirconium (IV) chloride, zirconium acetate, zirconium oxychloride, zirconium hydroxychloride, ammonium zirconium carbonate, and so on.

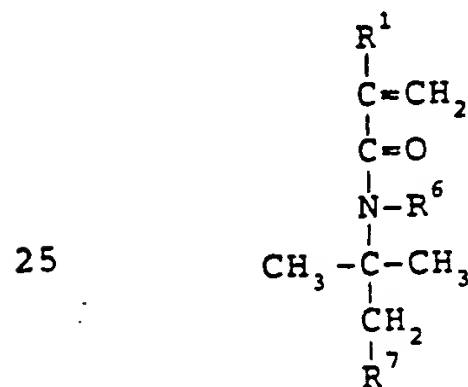
The preferred chelating compounds can be selected from:

(1) alkaline metal salts of acrylic or methacrylic acid having the structure:



where R^1 is described previously and M represents Li, Na, K, Rb, Cs, or NH_4 , preferably NH_4 , Na, or K;

(2) N-substituted acrylamido or methacrylamido monomers containing ionic groups having the structure:

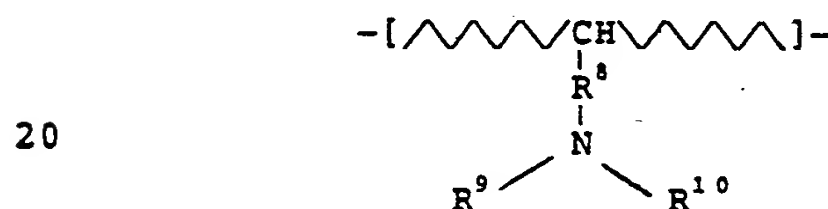


where R^1 is described previously, R^6 represents H or an alkyl group having up to four carbon atoms, preferably H, R^7 represents COOM or $-\text{SO}_3\text{M}$ where M is described previously;

(3) alkali metal salt of p-styrene sulfonic acid;

- (4) sodium salt of 2-sulfo ethyl acrylate and sodium salt of 2-sulfo ethyl methacrylate;
 (5) 2-vinyl pyridine and 4-vinyl pyridine;
 (6) vinyl imidazole;
 (7) N-(3-aminopropyl) methacrylamide
 5 hydrochloride; and
 (8) 2-acetoacetoxy ethyl acrylate and 2-acetoacetoxy ethyl methacrylate.

Other crosslinkable polymers suitable for the
 10 matrix component of the hydrophilic SIPNs of the present invention are polymers having crosslinkable tertiary amino groups, wherein said groups can be provided either as part of the monomeric units used in the formation of the polymer, or grafted onto the polymer after the formation
 15 of the polymeric backbone. These have the general structure of:

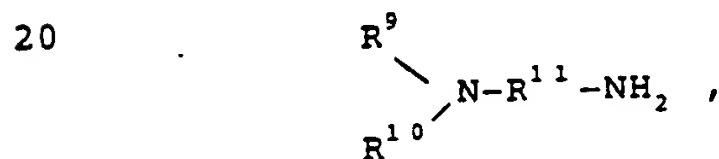


wherein R^8 represents a member selected from the group consisting of substituted and unsubstituted alkyl
 25 groups, substituted and unsubstituted amide groups, and substituted and unsubstituted ester groups, the foregoing groups preferably having no more than ten carbon atoms, more preferably having no more than five carbon atoms, substituted and unsubstituted aryl groups, preferably
 30 having no more than 14 carbon atoms, R^9 and R^{10} independently represent a member selected from the group consisting of substituted and unsubstituted alkyl groups, preferably having no more than ten carbon atoms, more preferably having no more than five carbon atoms, and
 35 substituted and unsubstituted aryl groups, preferably having no more than 14 carbon atoms. Additionally, R^9 and

R^{10} can be connected to form the substituted or unsubstituted cyclic structure $-R^9-R^{10}-$. The symbol \sim represents a plurality of unsubstituted or substituted $-CH_2-$ groups linked together to form the backbone of the chain.

5 Where water or other aqueous liquids are to be absorbed, it is preferred that R^8 be selected to be $-(C=O)NH(R^{11})-$, wherein R^{11} represents a substituted or unsubstituted divalent alkyl group, preferably having no more than ten carbon atoms, and more preferably having no
10 more than five carbon atoms. Preferred substituents for R^{11} are those capable of hydrogen bonding, including $-COOH$, $-CN$, and $-NO_2$. Additionally, R^{11} can include in its structure hydrogen bonding groups, such as $-CO-$, $-S=O$, $-O-$, $>N-$, $-S-$, and $>P-$.

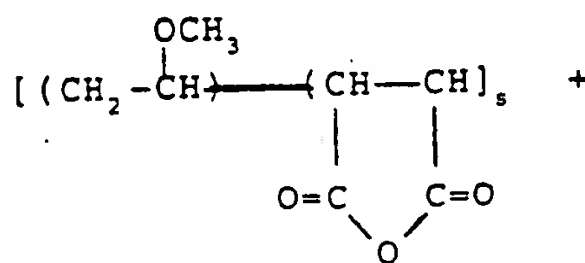
15 Crosslinkable polymers suitable for the matrix component wherein R^8 is $-(C=O)NH(R^{11})-$ can be prepared by treating polymers or copolymers containing maleic anhydride, with an amine having the structure:



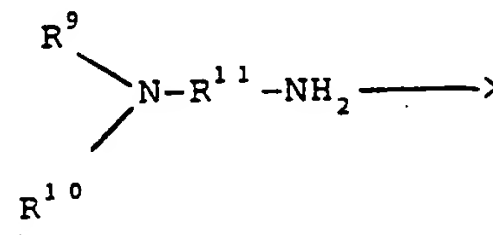
wherein, R^9 , R^{10} , and R^{11} are as described previously.

25 A particularly useful example of a crosslinkable matrix component is a copolymer of polymethyl vinyl ether and maleic anhydride, wherein these two monomeric units are present in approximately equimolar amounts. This copolymer can be formed in the following manner:

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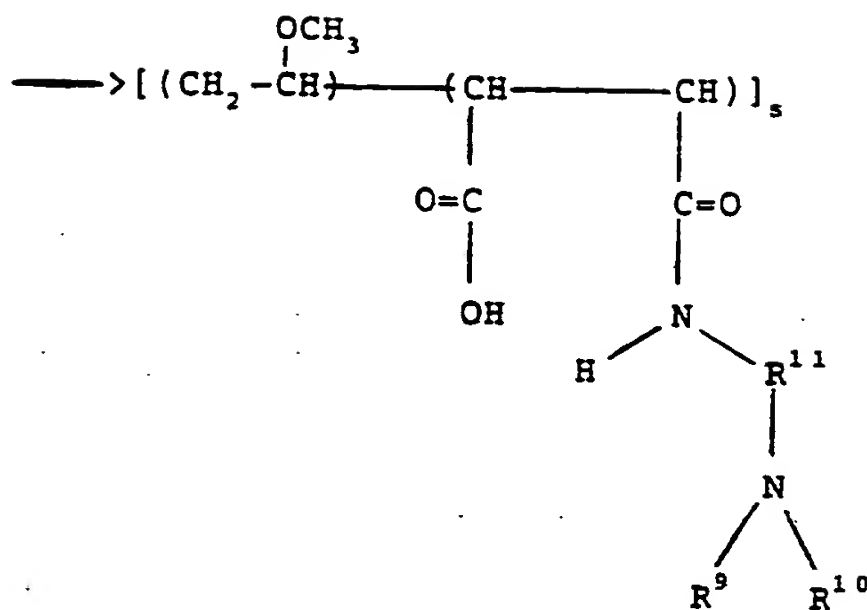
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(a)

(b)

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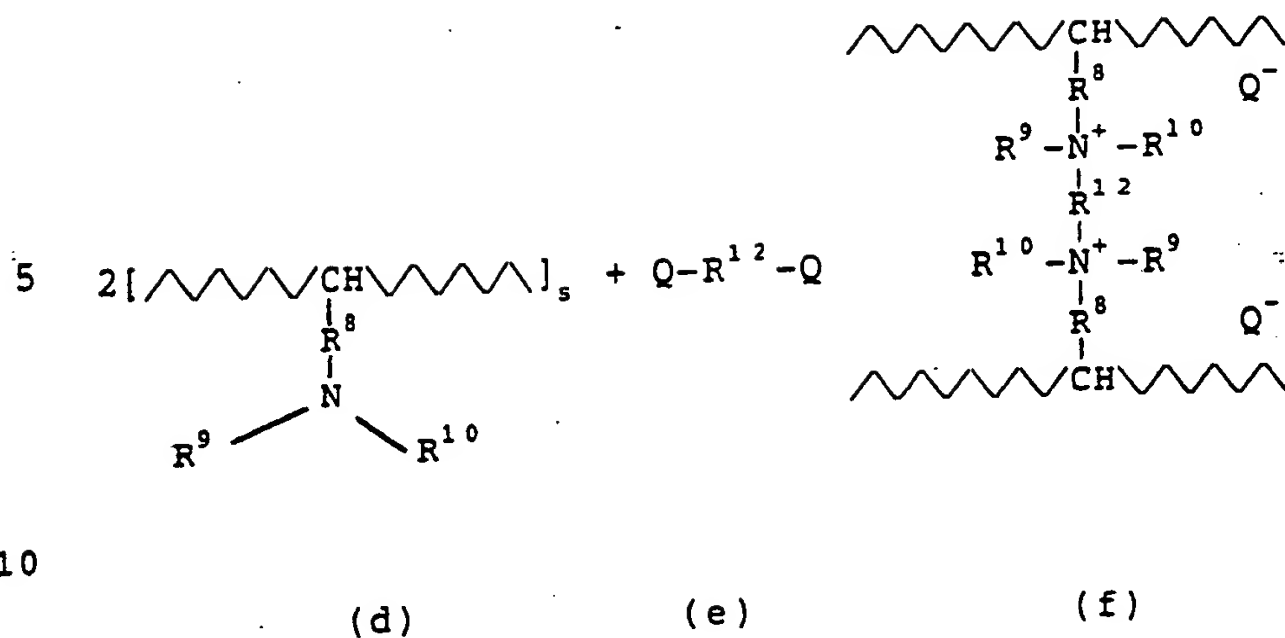


(c)

wherein R^9 , R^{10} , and R^{11} are as described previously, and s preferably represents a number from about 100 to about 600. This reaction can be conveniently performed by dissolving the polymethyl vinyl ether/maleic anhydride copolymer, i.e., reactant (a), in methyl ethyl ketone, dissolving the amine, i.e., reactant (b), in an alcohol, such as methanol or ethanol, and mixing the two solutions. This reaction proceeds rapidly at room temperature, with agitation. The product of this reaction may begin to form a cloudy suspension, which can be cleared by the addition of water to the solution.

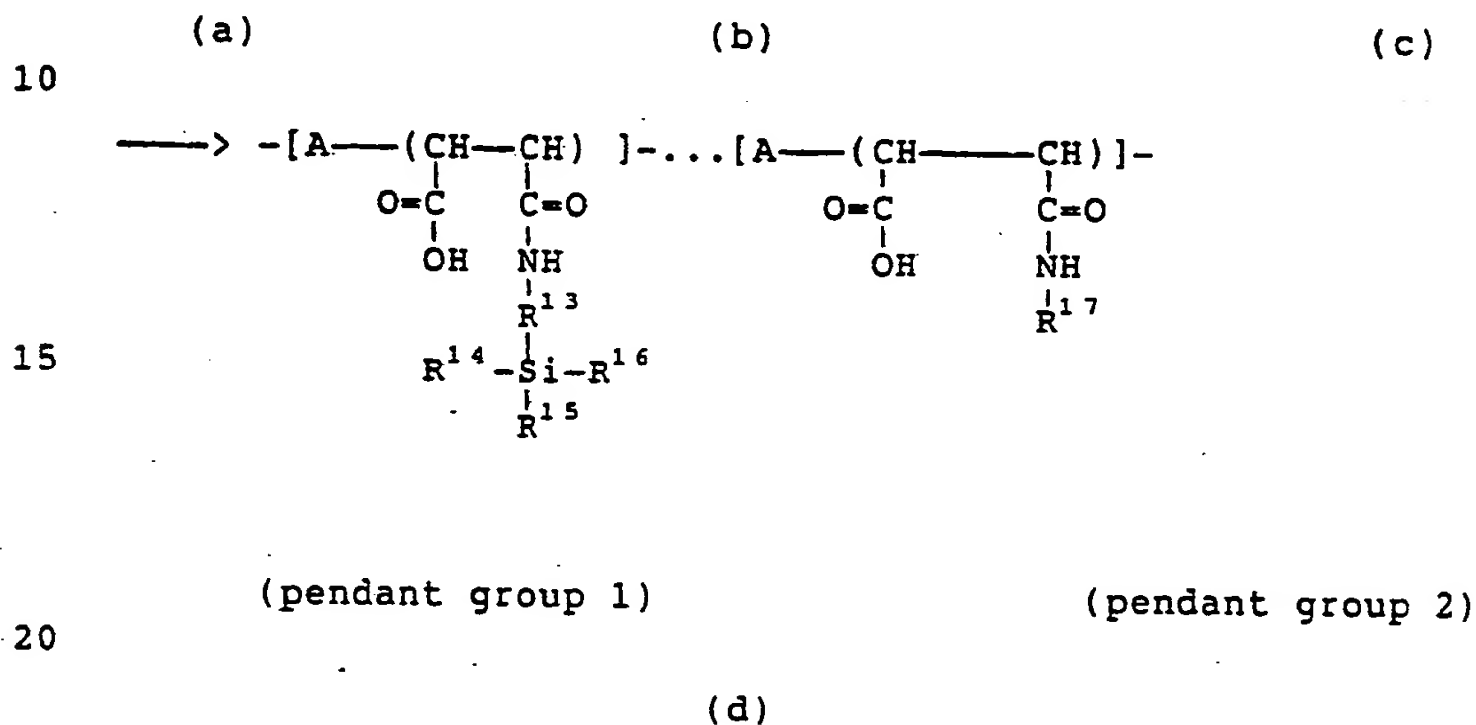
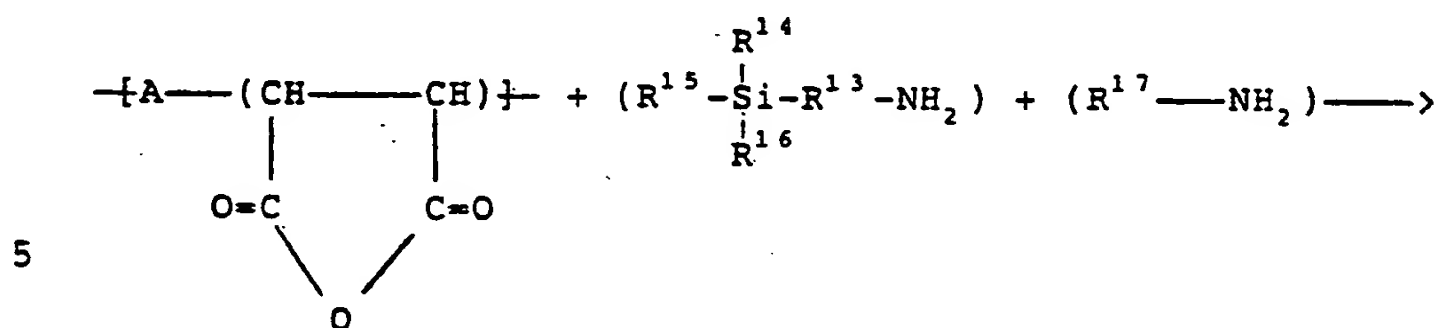
Crosslinking agents suitable for this type of polymer are multi-functional alkylating agents, each functional group of which forms a bond with a polymer chain through a tertiary amino group by quaternization of the trivalent nitrogen of the tertiary amino group. Difunctional alkylating agents are suitable for this purpose. In the case where the tertiary amino group is pendant to the backbone of the polymer, this crosslinking reaction can be depicted as follows:

35



where R^8 , R^9 , R^{10} , and s are as described previously, R^{12} can be the same as R^8 , R^9 , or R^{10} , and Q^- can be a halide, an alkyl sulfonate, preferably having no more than 5 carbon atoms, or any aryl sulfonate, preferably having no more than 14 carbon atoms.

Other crosslinkable polymers suitable for forming the matrix component of the SIPNs of the present invention include polymers having silanol groups, wherein the silanol groups can either be part of the monomeric units used in the formation of the polymer or be grafted onto the polymer after the formation of the polymeric backbone. If grafting is preferred, the polymeric backbones generally contain monomeric units of maleic anhydride, which can be converted into graftable sites by reaction with compounds having primary amino groups. Silanol side groups can be grafted onto these sites by heating a solution containing the backbone polymer with an aminoalkoxysilane. The alkoxysilane can subsequently be hydrolyzed by the addition of water. The reaction scheme can be depicted as follows:



wherein A represents a monomeric unit preferably selected from the group consisting of acrylonitrile, allyl acetate, ethylene, methyl acrylate, methyl methacrylate, methyl vinyl ether, stilbene, isostilbene, styrene, vinyl acetate, vinyl chloride, vinylidene chloride, vinylpyrrolidone, divinylether, norbornene, and chloroethyl vinyl ether;

R¹³ represents a divalent alkyl group, preferably having up to ten carbon atoms, more preferably having not more than five carbon atoms; R¹⁴, R¹⁵, and R¹⁶ independently represent alkoxy groups having up to about five carbon atoms, more preferably having not more than about three carbon atoms; and

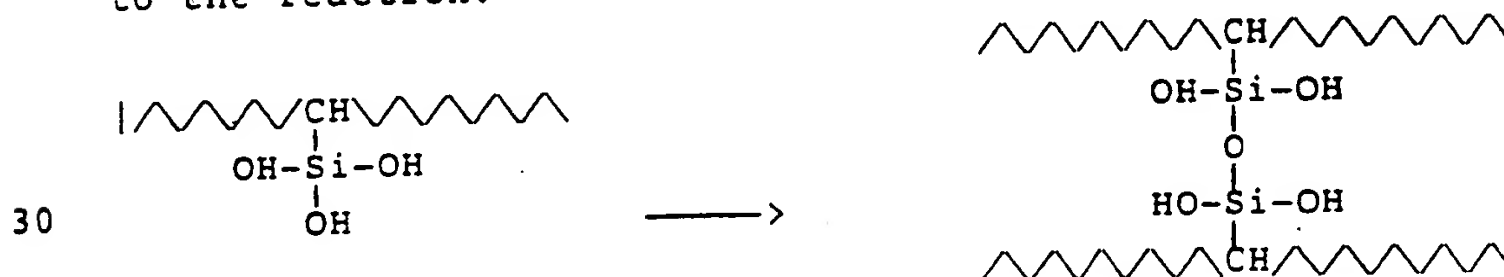
R^{17} represents a member selected from the group consisting of substituted or unsubstituted alkyl groups, preferably having up to ten carbon atoms, more preferably having not more than five carbon atoms, and substituted or unsubstituted aryl groups, preferably having up to 14 carbon atoms.

Suitable substituents for R^{17} include alkoxy, -OH, -COOH, -COOR, halide, and -NR₂, wherein R represents an alkyl group, preferably having up to five carbon atoms, more preferably having not more than three carbon atoms.

The relative amounts of the two types of side groups in polymer (d) are determined by the relative amounts of compounds (b) and (c) used in the grafting solutions. The molar ratio of compound (c) to compound (b) in the reaction ranges from about 3 to about 6, preferably from about 4 to about 5.

A discussion of the copolymerization of these monomeric units with maleic anhydride and the properties of the resulting copolymers can be found in Brownell, G. L., "Acids, Maleic and Fumaric," in Encyclopedia of Polymer Science and Technology, Vol. 1, John Wiley & Sons, Inc., (New York:1964), pp. 67-95.

Once the silanol groups are formed by hydrolysis, the resulting polymer can be crosslinked by the removal of water and other solvents from the system without addition of further crosslinking agent, according to the reaction:

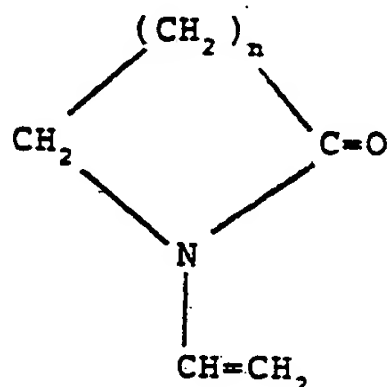


Additionally, crosslinking can occur at more than one of the -OH groups attached to the silicon atom.

While it is the primary function of the matrix

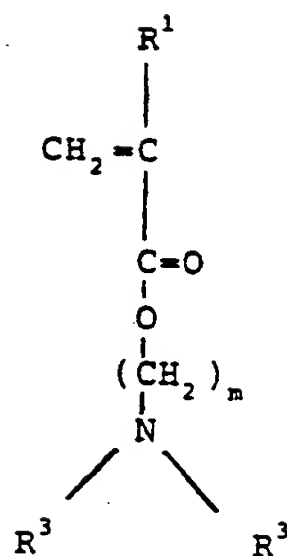
component of the SIPN to impart physical integrity and durability to the SIPN without adversely affecting the overall liquid absorbency of the SIPN, it is the primary function of the liquid-absorbent component to promote absorption of liquids. When aqueous liquids are to be absorbed, as is in the case of most inks, the liquid-absorbent component must be capable of absorbing water, and preferably be water-soluble. The liquid-absorbent component can be selected from polymers formed from the following monomers:

- (1) vinyl lactams having the repeating structure:



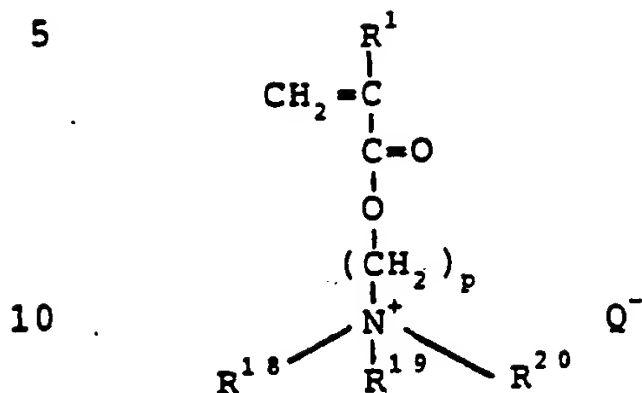
where n is as described previously;

- (2) alkyl tertiary amino alkylacrylates and alkyl tertiary amino alkylmethacrylates having the structure:



where m, R¹ and R³ are as described previously;

- (3) alkyl quaternary amino alkylacrylates or alkyl quaternary amino alkyl methacrylates having the structure:



where p represents the integer 1 or 2; and R¹ is as described previously, R¹⁸, R¹⁹, R²⁰ independently represent hydrogen or an alkyl group having up to 10 carbon atoms, preferably having from 1 to 6 carbon atoms, and Q represents a halide, R¹⁸SO₄, R¹⁹SO₄, or R²⁰SO₄.

Polymerization of these monomers can be carried out by conventional typical free radical polymerization techniques as mentioned previously.

Alternately, the liquid-absorbent component can be selected from commercially available water-soluble or water-swallowable polymers such as polyvinyl alcohol, polyvinyl alcohol/poly(vinyl acetate) copolymer, poly(vinyl formal) or poly(vinyl butyral), gelatin, carboxy methylcellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxyethyl starch, polyethyl oxazoline, polyethylene oxide, polyethylene glycol, polypropylene oxide, and so on. The preferred polymers are polyvinyl lactams, especially polyvinyl pyrrolidone, and polyvinyl alcohol.

SIPNs of the present invention to be used for forming ink-receptive layers typically comprise from about 0.5 to 6.0% by weight of crosslinking agent, preferably

from about 1.0 to 4.5% by weight, when crosslinking agents are needed. The crosslinkable polymer can comprise from about 25 to about 99% by weight, preferably from about 30 to about 60% by weight, of the total SIPNs. The liquid-absorbent component can comprise from about 1 to about 75% by weight, preferably from about 40 to about 70% by weight, of the total SIPNs. Such ink-receptive layers are generally borne by a substrate, such as transparent polymeric sheet. To form an ink-receptive layer, it is convenient to apply a composition for preparing such a layer to the substrate by means of a coating solution, which is subsequently dried to form a solid layer. A coatable liquid composition can be prepared by dissolving polymers of the matrix component and the liquid-absorbent component in a common solvent, which can be water, or water-miscible solvents, in appropriate proportions depending on the solubility of the components. The appropriate crosslinking agent, if used, is then added, and mixed until a uniform solution is obtained.

Common solvents can be selected by making use of Hansen parameters, which are numerical values that characterize the individual contributions to cohesive energy density made by the intermolecular dispersion forces, dipole forces, and hydrogen bonding forces of a particular compound. Soluble solid materials tend to be more readily dissolved by liquids having Hansen parameters within a specified range, this range being called the solubility envelope, and less readily dissolved by liquids having Hansen parameters outside of the solubility envelope. Because of this tendency, Hansen parameters can be used as a basis for selecting single solvents or for formulating solvent blends capable of dissolving a particular solid material or combination of solid materials.

Experimentally determined Hansen parameters and solubility envelopes for a variety of solid materials, along with Hansen parameters for many commonly used

solvents, as well as formulae for mathematically estimating Hansen parameters of materials not listed, can be found in Barton, A.F.M. CRC Handbook of Solubility Parameters and Other Cohesion Parameters CRC Press, Inc., (Boca Raton: 1983), incorporated herein by reference.

5 Systematic methods for utilizing Hansen parameters to compute formulations for solvent blends capable of dissolving particular combinations of solid materials in more complicated systems can be found in Teas, J.P., "Solubility Parameters", Treatise on Coatings,
10 R.R. Myers and J.S. Long, ed., Vol. 2, Part II, Marcel Dekker (New York: 1976), p. 413-448, incorporated herein by reference. Because such computational methods often result in more than one possible solvent formulation, additional experimental evaluation may be needed to arrive
15 at an optimal formulation.

Additional constraints upon the choice of solvents may arise from practical requirements involving coating, drying, toxicity, or other considerations.

20 While in solution prior to coating, little or no crosslinking of the matrix polymer takes place. The components remain uniformly dissolved in solution, retaining good coating characteristics without gelation and having adequate pot life to allow coating onto a transparent substrate, such as a polymeric film, and
25 subsequent drying to form a continuous layer. The amount of heat required to accomplish the drying in a reasonable time is usually sufficient for causing crosslinking of the matrix component to occur. In this way, the problems of dealing with volatile monomers, some of which can be
30 toxic, and unreacted monomers resulting from incomplete conversion are eliminated.

SIPN solutions of the present invention may contain additional modifying ingredients such as adhesion promoters, particles, surfactants, viscosity modifiers,
35 and like materials, provided that such additives do not adversely affect the liquid-absorbing capability of the invention.

Coating can be conducted by any suitable means, such as knife coating, rotogravure coating, reverse roll coating, or other conventional means. Drying can be accomplished by means of heated air. If preferred, an adhesion promoting priming layer can be applied to the substrate prior to coating. Such priming layers can include primer coatings, surface treatments such as corona treatment, or other appropriate treatment. Adhesion of the SIPN layer can also be promoted by providing a gelatin sublayer of the type used in photographic film backings between the priming layer and the SIPN layer. Film backings having both a priming layer and a gelatin sublayer are commercially available, and are frequently designated as primed and subbed film backings.

When the SIPNs of the present invention are to be used to form the ink absorbing layer of a film for use with an ink-jet printer, it is preferred that the backing of the film have a caliper in the range of about 50 to about 125 micrometers. Films having calipers below about 50 micrometers tend to be too fragile for graphic arts films, while films having calipers over about 125 micrometers tend to be too stiff for easy feeding through many of the imaging machines currently in use. Materials suitable for backings for graphic arts films include polyesters, e.g., polyethylene terephthalate, cellulose acetates, polycarbonates, poly(vinyl chlorides), polystyrenes, and polysulfones.

When the SIPNs of the present invention are to be used to form the ink absorbing layer of a film for use with an ink-jet printer, the SIPN layer may further be overcoated with an ink-permeable, anti-tack protective layer, such as, for example, a layer comprising polyvinyl alcohol in which starch particles have been dispersed, or a semi-interpenetrating polymeric network in which polyvinyl alcohol is the absorbent component. Such overcoat layers can provide surface properties that help to properly control the spread of ink droplets so as to optimize image quality.

In addition to the polymeric materials comprising the SIPN, other modifying ingredients, such as surfactants; particles, or the like, can be added to the formulation for the overcoat layer to improve ink flow, dot spread; or other aspects of ink receptivity to improve image appearance.

In order to more fully illustrate the various embodiments of the present invention, the following non-limiting examples are provided.

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Example 1

A polymeric material suitable for the matrix of an SIPN was prepared by combining N-vinyl-2-pyrrolidone (75 parts by weight), N,N-dimethyl acrylamide (2 parts by weight), the ammonium salt of acrylic acid (5 parts by weight), azo-bis-isobutyronitrile (0.14 part by weight, "Vazo", available from E. I. DuPont de Nemours and Company), and deionized water (566 parts by weight) in a one-liter brown bottle. The mixture was purged with dry nitrogen gas for five minutes; polymerization was then effected by immersing the bottle for between 18 to 24 hours in a constant temperature bath maintained at a temperature of 60°C. The resulting polymerized mixture was then diluted with deionized water to give a 10% aqueous solution. The resulting solution will hereinafter be called Solution A.

Solution A (8 g of a 10% aqueous solution) was mixed with surfactant (0.2 g of a 2% aqueous solution, "Triton X100", Rohm and Haas Co.), polyvinyl alcohol (8 g of a 5% aqueous solution, "Vinol 540", Air Products and Chemicals, Inc.), and polyfunctional aziridine crosslinking agent (0.5 g of a 10% aqueous solution, XAMA-7, Sannacor Ind. Inc.) in a separate vessel.

The resultant solution was coated onto a backing of polyethylene terephthalate film having a caliper of 100 micrometers, which had been primed with polyvinylidene chloride, over which had been coated a gelatin sublayer of

the type used in photographic films for improving gelatin adhesion ("Scotchpar" Type PH primed and subbed film, available from Minnesota Mining and Manufacturing Company). Coating was carried out by means of a knife coater at a wet thickness of 200 micrometers. The coating was then dried by exposure to circulating heated air at a temperature of 90°C for five minutes to form a clear SIPN layer.

Printing was performed with an ink-jet printer and pen using ink containing Direct Blue 99 dye (3% solution in water). After six minutes, the imaged film was immersed in water and no dye was removed from image. The SIPN layer remained intact.

Example 2

A solution of matrix component of the present invention was prepared by first dissolving 1.3 g of a copolymer of methyl vinyl ether and maleic anhydride ("Gantrez" AN-169, available from GAF Chemicals Corporation) in 24.6 g of methyl ethyl ketone. In a separate vessel, 1.3 g of aminopropyl morpholine (available from Aldrich Chemical Company, Inc.) were dissolved in 11.6 g of methanol. The previously prepared solution of copolymer was then added, dropwise, to the aminopropyl morpholine/methanol solution, after which 36.6 g of distilled water were added to the resulting combined solutions. The resulting solution will hereinafter be called matrix component Solution B.

In yet another vessel, 2.5 g of polyvinyl pyrrolidone (K90, available from GAF Chemicals Corporation) were dissolved in 22.1 g of distilled water. This solution was then added to matrix component Solution B and agitated until a uniform solution was obtained. The resulting solution, hereinafter called blend Solution B, was then divided into 5 samples of 20.0 g each.

The dihalo compound 3,3-bis-(iodomethyl)-oxetane was prepared according to the procedure described in

Sorenson, W.R., and Campbell, T.W., Preparative Methods of Polymer Chemistry, 2nd Edition, New York, Interscience Publishers, Inc., 1968, p. 376, incorporated herein by reference. A solution of 10 parts by weight of this compound and 90 parts by weight of dimethyl formamide (DMF) was prepared for use as an alkylating agent for crosslinking the matrix component.

Crosslinkable solutions according to the present invention were prepared by adding 0.35 g of the 3,3-bis-(iodomethyl)-oxetane/DMF solution to one of the 20.0 g samples of blend Solution B, 0.70 g of the 3,3-bis-(iodomethyl)-oxetane/DMF solution to a second 20.0 g sample of blend Solution B, and 1.4 g of the 3,3-bis-(iodomethyl)-oxetane/DMF solution to a third 20.0 g sample of blend Solution B.

These solutions were each coated onto a backing of polyethylene terephthalate film having a caliper of 100 micrometers which had been primed with polyvinylidene chloride, over which had been coated a gelatin sublayer of the type used in photographic films for improving gelatin adhesion ("Scotchpar" Type PH primed and subbed film, available from Minnesota Mining and Manufacturing Company). Coating was carried out by means of a knife coater, with the wet thickness of the solution coated onto the film being 75 micrometers. Drying was carried out by exposure to circulating heated air at a temperature of 90°C for five minutes.

After drying, all three of the solutions resulted in clear SIPN layers that retained their physical integrity when washed with a moving stream of water at room temperature. Exposure to water in selected areas resulted in detectable water absorption, as indicated by swelling of the SIPN layer. Swelling of the SIPN layer was detected by the bump that could be felt by running a finger over the surface of the coated film in such a way as to pass from the portion of the layer not exposed to water to the portion that was exposed to water. Because

the amount of crosslinking agent used could be varied over a wide range without failure of crosslinking and without loss of hydrophilicity, it was concluded that this type of crosslinking is sufficiently tolerant of variability to be useful in a manufacturing process.

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Example 3

The polymeric material for the matrix of the SIPN was prepared by combining N-vinyl-2-pyrrolidone (28 parts by weight), N,N-dimethyl acrylamide (20 parts by weight), 2-acrylamido-2-methyl propanesulfonic acid (2 parts by weight of the ammonium salt), azo-bis-isobutyronitrile (0.07 part by weight, "Vazo", available from E. I. du Pont de Nemours and Company), and deionized water (280 parts by weight) in a one-liter brown bottle. After the mixture was purged with dry nitrogen gas for five minutes, polymerization was effected by immersing the bottle in a constant temperature bath maintained at 60°C for eight hours to give a very viscous clear solution (97.8% conversion). The resulting polymerized mixture was then diluted with deionized water to give a 10% solution in water, hereinafter called Solution C.

Solution C (21.94 g of a 10% aqueous solution) was thoroughly mixed with polyvinyl alcohol ("Vinol 540", available from Air Products and Chemical, Inc., 28.6 g of a 5% aqueous solution), and chromium chloride crosslinking agent (0.29 g of a 10% aqueous solution) in a separate vessel. The resultant solution was coated onto a backing of polyethylene terephthalate film having a caliper of 100 micrometers, which had been primed with polyvinylidene chloride, over which had been coated a gelatin sublayer of the type used in photographic films for improving gelatin adhesion ("Scotchpar" Type PH primed and subbed film, available from Minnesota Mining and Manufacturing Company). Coating was carried out by means of a knife coater at a wet thickness of 200 micrometers. The coating

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was then dried by exposure to circulating heated air at a temperature of 90°C for five minutes. After drying, a clear SIPN layer formed.

Printing was performed with an ink-jet printer and a pen plotter using ink containing dye (3 to 5% solution in water). After one minute, the imaged film was dry to the touch. The SIPN layer remained intact.

Example 4

The purpose of this example is to illustrate the use of an SIPN of the present invention as a single layer hydrophilic coating that is capable of absorbing aqueous ink.

A solution of the grafting material was prepared by first dissolving 0.07 g of 3-aminopropyltriethoxysilane (Aldrich Chemical Co., Inc.) and 0.22 g of 2-methoxyethylamine (Aldrich Chemical Co., Inc.) in 7.9 g of methanol. In a separate vessel, a solution of the backbone polymer was prepared by dissolving 0.5 g of a copolymer of methyl vinyl ether and maleic anhydride ("Gantrez AN-169", GAF Chemicals Corporation) in 9.5 g of methyl ethyl ketone. The solutions of the grafting material and the backbone polymer were then combined and stirred to provide a clear, viscous liquid. A solution of absorbent component was prepared in a separate vessel by adding 1.5 g of polyvinyl pyrrolidone, (K-90, GAF Chemicals Corporation) to 13.5 g of deionized water and stirring the resulting mixture until a clear solution was formed. The solution of absorbent component, along with 15.0 g of water, was added to the previously prepared combined solutions of grafting material and backbone polymer, and the resulting mixture stirred at room temperature until a clear solution was obtained.

An ink-receptive layer was formed by coating the solution so prepared onto a sheet of polyvinylidene chloride-primed and gelatin-subbed polyethylene terephthalate film having a caliper of 100 micrometers

5 ("Scotchpar" Type PH primed and subbed film, available from Minnesota Mining and Manufacturing Company) by means of a knife coater adjusted so as to apply a liquid layer having a wet thickness of 125 micrometers. The liquid layer was dried in a forced air oven at a temperature of 90°C for a period of five minutes.

10 The ink receptivity of the dried coating was tested by writing on it with a pen which used an aqueous ink ("Expresso" brand pen, Sanford Corp. Bellwood, IL). The ink image dried sufficiently in 10 seconds to be non-smearable when gently rubbed with the finger. The SIPN layer tended to become tacky at relative humidities of about 90% or greater.

15 Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

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WHAT IS CLAIMED IS:

1. An article comprising a substrate bearing on at least one major surface thereof a hydrophilic liquid-absorbent, semi-interpenetrating network formed from a polymer blend comprising:
- 5 (a) at least one crosslinkable polymer; and
- (b) at least one liquid-absorbent polymer comprising a water-absorbent polymer.
- 10 2. The article of Claim 1, wherein said crosslinkable polymer is crosslinked after it has been applied to said substrate.
- 15 3. Method of preparing the article of Claim 1, comprising the steps of:
- (1) blending said at least one crosslinkable polymer with said at least one liquid-absorbent polymer in a liquid medium to
- 20 form a solution;
- (2) applying said solution to said substrate; and
- (3) drying said solution,
- whereby said crosslinkable polymer becomes crosslinked.
- 25 4. The article of Claim 1, further including a crosslinking agent.
5. The article of Claim 4, wherein said
- 30 crosslinkable polymer is crosslinked after it has been applied to said substrate.
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6. Method of preparing the article of Claim 4, comprising the steps of:

(1) blending said at least one
crosslinkable polymer with said at least one
liquid-absorbent polymer and a crosslinking
agent in a liquid medium to form a solution;

(2) applying said solution to said
substrate; and

(3) drying said solution,
whereby said crosslinkable polymer becomes crosslinked.

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I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 B41M5/00

II. FIELDS SEARCHEDMinimum Documentation Searched⁷

Classification System

Classification Symbols

Int.Cl. 5

B41M

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸**III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹**Category¹⁰Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²Relevant to Claim No.¹³

A

EP,A,0 365 307 (3M) 25 April 1990
see claims 1-17

1-6

¹⁰ Special categories of cited documents : ¹⁰

- ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the Actual Completion of the International Search

18 FEBRUARY 1992

Date of Mailing of this International Search Report

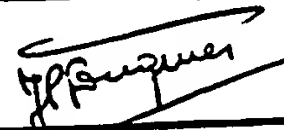
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9106686
SA 53266**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on:
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0365307	25-04-90	US-A- 4935307	19-06-90
		AU-A- 4175489	26-04-90
		JP-A- 2208366	17-08-90
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